

Original Article

# Vaporization and Conversion of Ethanolamines used in Metalworking Operations

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**Objectives:** This study examined how ethanolamines (EAs) with the same functional alcohol group ( $\text{HOCH}_2\text{CH}_2$ ), such as mono-EA (MEA), di-EA (DEA), and tri-EA (TEA), in water-based metalworking fluids (wbMWFs) are vaporized, condensed, and transformed by heat generated during metalworking.

**Methods:** Two types of experimental apparatus were manufactured to achieve these objectives.

**Results:** Vaporization tests using a water bath showed that the vaporization rate increased markedly from  $0.19 \text{ mg/m}^2\text{-min}$  at  $23.5^\circ\text{C}$  to  $8.04 \text{ mg/m}^2\text{-min}$  at  $60^\circ\text{C}$ . Chamber tests with a heat bulb revealed that "spiked" MEA was fully recovered, while only 13.32% of DEA and no TEA were recovered. Interestingly, non-spiked types of EAs were detected, indicating that heat could convert EAs with more alcohol groups (TEA or DEA) into other EAs with fewer group(s) (DEA or MEA). The EA composition in fresh fluid was 4% DEA, 66% TEA, and 30% MEA, and in used fluids ( $n = 5$ ) was 12.4% DEA, 68% TEA, and 23% MEA. Conversion from TEA into DEA may therefore contribute to the DEA increment. Airborne TEA was not detected in 13 samples taken from the central coolant system and near a conveyor belt where no machining work was performed. The DEA concentration was  $0.45 \text{ mg/m}^3$  in the only two samples from those locations. In contrast, airborne MEA was found in all samples ( $n = 53$ ) regardless of the operation type.

**Conclusion:** MEAs easily evaporated even when MWFs were applied, cleaned, refilled, and when they were in fluid storage tanks without any metalworking being performed. The conversion of TEA to DEA and MEA was found in the machining operations.

**Key Words:** Water-soluble fluids, Ethanolamine (EA), Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), Metalworking fluids (MWF)

## Introduction

Metalworking fluids (MWFs) are generally classified into four types (straight, soluble, synthetic, and semi-synthetic) according to the amount and type of oil that they contain.

In broad terms, there are essentially two types of MWFs: oil-based (straight) and water-based MWFs (wbMWFs; solu-

ble, synthetic, and semi-synthetic). Alkanolamines or ethanolamines (EAs) - triEA (TEA), di-EA (DEA), and mono-EA (MEA) - have been added as integral components to wbMWFs, but not straight fluids, to stabilize the pH or inhibit corrosion [1,2].

EAs have the potential to act as a respiratory irritant and a sensitizing agent [3,4]. Amino alcohols (alkanolamines) are derivatives of ammonia in which one, two, or three (alkanol) groups are attached to one amino ( $\text{NH}^3$ ) group; the respective EAs are monoEA ( $\text{HOCH}_2\text{CH}_2\text{NH}_2$ ), diEA( $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ ), and triEA( $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ ). EAs are strong bases [4] and can appear simultaneously both as aerosol and vapor in the workplace atmosphere because of the broad range of vapor

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pressures. EAs generally have low vapor pressures, and this reduces the inhalation hazard in industry [5]. No study has been conducted to examine the effect of the high temperatures generated during metalworking operations on the physical and chemical properties of EAs in fluid formulations.

The ultimate purpose of this study was to examine the variations among EAs in wbMWFs through both experimental and field studies. The specific objectives were: 1) to examine through experimental tests how they are evaporated, condensed and converted as temperatures rise; 2) to compare fluid EA levels between fresh and used fluids taken from machining operations; and 3) to assess airborne EA levels among several types of machining operations. EA levels measured in bulk fluid and air were evaluated to supplement the results obtained from experimental testing.

## Materials and Methods

### Experimental study

Two types of experimental apparatuses were designed in order to generate temperatures higher than room temperature. Each experiment was repeated three times under the same conditions.

MEA, DEA, and TEA were diluted to 1% with de-ionized water (DI), which falls in the range used in machining operations. The water temperature in the thermostat-controlled baths was kept at 23.5°C, 40°C, 50°C, or 60°C to evaluate the EA vaporization as the temperature rose. Two-thirds of the evaporation tube containing 5 mL EA was immersed in the water bath. Vaporized EA was absorbed into the DI using an impinger with air drawn by a personal pump (model MSA 87004, MSA, U.S.A.) for one hour. The surface area in the immersed tube was  $0.001256 \text{ m}^2$  ( $20 \times 20 \text{ mm} \times \pi$ ) and the evaporation rate was given as  $\text{mg}/\text{m}^2 \text{ per surface} \cdot \text{min unit}$ .

A glass chamber with a 60 mm diameter was constructed. A heating coil was built inside the chamber to create sufficiently high temperatures to vaporize all EAs. One hundred 100  $\mu\text{L}$  of each EA at concentrations of 1% were injected onto the heating coil inside the chamber using a micro-syringe. A mixture solution containing each EA at a concentration of 1% was also tested. Fresh air was allowed into the chamber and was taken up into the impinger over 20 minutes in order to collect the vaporized EAs (Fig. 1). After the air was removed, the glass bulb was completely rinsed with DI. The EA content in the rinse solution was also analyzed to account for EAs that had been left inside the glass chamber.

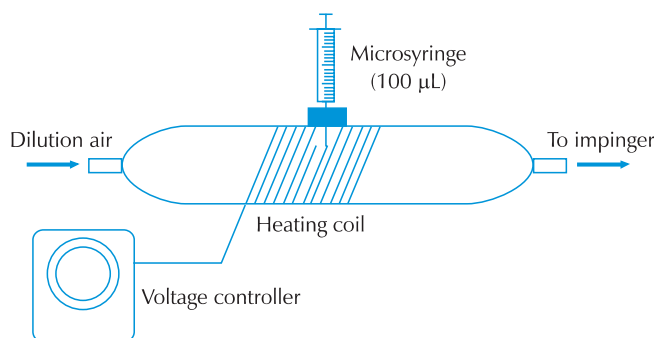


Fig. 1. Glass chamber test system.

### Field study

Synthetic and soluble MWFs were found to be used in machining of automotive parts, such as cylinder blocks, con-rods, cylinder heads, crank shafts, and cam shafts. EA information in the Material Safety and Data Sheets (MSDS) was examined. The EA composition in the fluid that had been used in the machining operations described above was analyzed to compare with the content of each EA in the fresh fluid. Using the impinger, airborne EAs were taken not only from vaporization tests and sites of machining operations (milling, grinding, boring, drilling, and washing), but also from the central coolant system (CCS) and near conveyor belts. Airborne EAs were taken into the DI in an impinger near the machining operations for a long enough duration to be able to show the representative EA level and then the levels were measured separately. The impinger was completely rinsed with DI to collect any EA that may have adsorbed or attached to the inner wall of the inlet tube.

For machining operations, the used bulk fluid was taken from a flowing stream at the cutting points of each machine, when the circulation system was in operation. If the system was not in operation, the MWF circulation system was run for at least 10 minutes prior to sampling. The fresh fluid that had never been used was also collected. The fluid bulk sample was collected in a 50-ml sterile, tissue-culture grade centrifuge tube (Fisher Scientific cat. #05-538-55, USA).

Portions of the liquid samples from the impinger and centrifuge tube, respectively, were filtered using a micro-syringe with a 0.4  $\mu\text{m}$  pore-size filter, and were quantified by ion chromatography (Water 717 plus auto sampler, Waters Corporation) using an IC PAK<sup>TM</sup> C M/D guard column (Alltech, Lexington, KY), an IC PAK<sup>TM</sup> Cation M/D column ( $3.9 \times 150 \text{ mm}$  WAT 036570, Alltech) and a 432 conductivity detector (Waters Corporation). The eluent (0.1 mM EDTA and 2 mM nitric acid) was filtered through a 47 mm diameter, 0.45

um pore-size, Super 450 membrane filter (Waters Corporation), and sonicated (Model 3210, Branson, Danbury, Conn.) for 40 minutes to remove dissolved air. Samples for quantification were diluted to achieve optimum levels for analysis. The collection and quantification of EAs in fluid and air were based on the methods recommended by Krol et al. [6] (Table 1). The NIOSH method 3509 has been the only one in the field to quantify all three specified EAs (MEA, DEA, and TEA) simultaneously. This method uses a midjet impinger containing 15 mL of 2 mM hexanesulfonic acid (HSA) that is not convenient to obtain due to the lack of distributor information in the

catalog. Our sampling and analytical method used DI instead of HAS to collect airborne MEA, DEA, and TEA simultaneously, which was based on the method recommended by Krol et al. [6]. The validation for this method will be discussed in the results and discussion section.

## Results

### Evaporation, condensation and transformation of EAs in experimental tests

Vaporization tests using the thermostat-controlled baths re-

**Table 1.** Sampling and analytical methods for quantification of ethanolamines (EAs)

Absorbent solution for impinger	De-ionized water (18 mΩ)
Analytical system (apparatus)	Waters corporation ion chromatography
	Detector: waters 432 conductivity detector
	Separator: waters cation M/D column
	Guard column: cation M/D guard column
	Mobile phase : 2 mM nitric acid-0.1 mM EDTA
	Flow rate : 1.0 ml/min
Retention time	5-10 min
EDTA: ethylene diamine tetra acetic acid.	

**Table 2.** Evaporation rate of monoethanolamine (MEA) by temperature of the water bath

Classification		23.5°C	40°C	50°C	60°C
Amount/sample (g)	1 <sup>st</sup> round	12.81	81.40	140.00	709.53
	2 <sup>nd</sup> round	15.83	81.69	282.21	574.34
	3 <sup>rd</sup> round	13.78	91.00	386.09	534.89
Mean (g)		14.14	84.70	269.43	606.25
RSD (%)		10.89	6.45	45.85	15.11
Evaporation rate (mg/m <sup>2</sup> /min)*		0.19	1.12	3.58	8.04

Diethanolamine and triethanolamine did not evaporate in the temperature range tested.

RSD: relative standard deviation.

\*Evaporation rate by surface area in the immersed tube ( $r = 20$  mm, area = 0.01256 m<sup>2</sup>).

**Table 3.** Recovery rate (%) in evaporation tests using a glass chamber equipped with a heating coil

Round	MEA injected			DEA injected			TEA injected			Mixture of MEA, DEA and TEA injected		
	MEA	DEA	TEA	MEA*	DEA*	TEA	MEA <sup>†</sup>	DEA <sup>†</sup>	TEA	MEA <sup>‡</sup>	DEA <sup>‡</sup>	TEA
1	96.95	ND	ND	9.81	11.94	ND	8.26	12.92	ND	95.30	17.47	ND
2	94.75	ND	ND	10.42	12.53	ND	7.46	18.19	ND	98.38	24.49	ND
3	103.88	ND	ND	8.91	15.65	ND	7.25	13.86	ND	100.04	26.06	ND
Mean	98.53			9.71	13.37		7.65	14.99		97.91	22.67	
RSD	4.84			7.85	14.92		6.94	18.74		2.45	20.17	

MEA: monoethanolamine, DEA: diethanolamine, TEA: triethanolamine, ND: Not detected, RSD: relative standard deviation.

\*Weight as a percentage of the weight of DEA injected.

<sup>†</sup>Weight as a percentage of the weight of TEA injected.

<sup>‡</sup>Weight as a percentage of the weight of each ethanolamine injected.

vealed that vaporization of MEA increased as the temperature of the water bath increased, while no evaporation of DEA or TEA at less than 60°C was detected. Vaporization of MEA was detected even at 23.5°C. The vaporization rate of MEA increased markedly from 0.19 mg/m<sup>2</sup> · min at 23.5°C to 3.58 mg/m<sup>2</sup> · min at 50°C, and to 8.04 mg/m<sup>2</sup> · min at 60°C (Table 2).

Recovery of EAs spiked into the heat bulb inside the glass chamber under conditions of extreme heat was tested. The recovery rate for MEA ranged from 94.8% to 103.9%, indicating that most of the injected MEA was fully recovered and that the reliability of our sampling and analytical method was validated.

Only 13.4% of the injected DEA was recovered, while MEA was detected even though it had not been injected. In experiments involving injection of TEA only, no TEA was detected; however, both MEA and DEA were detected. Some 15.0% and 7.7% of injected TEA was assumed to have been converted into DEA and MEA, respectively. The results using the mixed samples showed a similar trend with more MEA being detected than had been originally added. Interestingly, much of the DEA and TEA was detected in the rinse solution after the vaporization experiment, while no MEA was recovered at that stage (Table 3). These experiments showed that, under very high temperatures, portions of the EAs with more alcohol groups (TEA or DEA) were transformed into EAs with fewer alcohol groups (DEA or MEA). In addition, a certain amount of DEA and TEA was found to condense again immediately

after vaporization. The exact amounts involved and the temperature at which condensation occurred were not tested.

### EA level in bulk fluids

The presence and relative amounts of specific EAs were not indicated in the MSDS, although EAs were detected both in fresh and bulk fluids (Table 4, 5).

In the fresh synthetic fluid (brand name: 39-154 = G), the TEA level was the highest among the EAs (10.17%), followed by MEA (4.64%) and DEA (0.63%). This order of bulk concentration was found in the five used fluids (Table 5). A great reduction in total EA level was recorded, from 15.4% in fresh fluids to 2.34% (mean) in the five used fluids. The degree of reduction might vary slightly depending on the duration of fluid use and the operation type.

The proportion of each EA as a percentage of total EA was compared between the fresh (G) and the used fluids (G1-G5). The fresh fluid EA composition was 30% MEA, 4% DEA, and 66% TEA. This is similar to the results of Kenyon et al, who reported that in fresh fluids, the average percentage of DEA in terms of total EA was the lowest (8.7%), followed by MEA (31%; n = 4), and then TEA (69%; n = 6). The average DEA composition was found to increase to 12% in used fluids, while TEA proportions did not exhibit a substantial difference (68% versus 66%). In contrast, MEA composition in the used fluid declined to 23%. These results indicate that the proportion of DEA may increase due to conversion (or change) from

**Table 4.** Comparison of ethanolamine content (%) in used fluid with those reported in the Material Safety and Data Sheets (MSDS)

Fluid type (brand name)	EA concentration, % (proportion of each EA as a percentage of total EA)						Total EA
	MSDS			Used fluid			
	MEA	DEA	TEA	MEA	DEA	TEA	
Soluble (799AL)	0	0	0	< LOD (0)	0.09 (56.3)	0.07 (43.8)	0.16
Soluble (713SK)	< 5	< 10	< 15	0.54 (17.9)	0.19 (6.3)	2.37 (78.7)	3.01
Soluble (Hysol)	Amine < 15			0.61 (75.3)	0.10 (12.3)	0.10 (12.3)	0.81
Synthetic (850K)	Alkanolamine < 20			0.20 (23.0)	0.63 (72.4)	0.04 (4.6)	0.87
Synthetic (CL310)	Alkanolamine < 30			0.25 (10.0)	0.84 (33.7)	1.40 (56.2)	2.49
Synthetic (EZ40)	Alkanolamine < 10			0.31 (75.6)	0.05 (12.2)	0.05 (12.2)	0.41
Synthetic (39-154)	Amine > 20			0.58 (24.0)	0.21 (8.7)	1.63 (67.4)	2.42
Synthetic (cimtech)	15-25		5-15	0.05 (3.1)	0.57 (35.4)	0.99 (61.5)	1.61
Washing fluid (5380)	Alkanolamine 8-10			0.05 (6.0)	0.32 (38.1)	0.47 (56.0)	0.84
Washing fluid	Amine complex 30 corrosion inhibitor 15			0.09 (4.5)	0.81 (40.1)	1.12 (55.4)	2.02

MEA: monoethanolamine, DEA: diethanolamine, TEA: triethanolamine.

Total EA: MEA + DEA + TEA, ( ): the proportion of each EA as a percentage of total EA.

**Table 5.** Comparison of content and proportion (%) of ethanolamine between fresh and used fluid

Fluid type	Type of machining	Period in use	Fluid EA level (each EA as a percentage of total EA)				Ratio (used/fresh)			
			MEA	DEA	TEA	Total EA	MEA	DEA	TEA	Total EA
G-fresh*	-	Fresh	4.61 (30.1)	0.63 (4.1)	10.17 (65.9)	15.44				
G 1	Drilling	Over 2 years	0.47 (24.5)	0.17 (8.9)	1.28 (66.7)	1.92	0.10	0.27	0.13	0.12
G 2	Milling	About 1 year	0.58 (24.0)	0.21 (8.7)	1.63 (67.1)	2.42	0.12	0.33	0.16	0.16
G 3	Drilling	About 3 years	0.33 (17.5)	0.23 (12.2)	1.33 (70.4)	1.89	0.07	0.37	0.13	0.12
G 4	Drilling	About 2 years	0.77 (23.1)	0.30 (9.0)	2.26 (67.9)	3.33	0.16	0.48	0.22	0.22
G 5	Boring	Over 3 years	0.54 (25.5)	0.18 (8.5)	1.40 (66.0)	2.12	0.12	0.28	0.14	0.14
Mean (G 1-G 5)			0.54 (23.1)	0.29 (12.3)	1.58 (67.5)	2.34	0.12	0.34	0.16	0.15
RSD (G 1-G 5)			29.43	24.12	25.51	25.33	29.43	24.12	25.51	25.33

MEA: monoethanolamine, DEA: diethanolamine, TEA: triethanolamine, RSD: relative standard deviation.

Total EA: MEA + DEA + TEA.

\*Synthetic fluid with brand name "39-154" from Table 4.

**Table 6.** Airborne ethanolamine levels taken from machining operations or areas

Operation	Sample no.	Fluid temp. (°C)	Ethanolamine level, mg/m <sup>3</sup> (RSD)			
			MEA	DEA	TEA	Total
Machining*	21*	31 (0.02)	0.11 (0.59)	0.08 (1.35)	0.16 (1.39)	0.36 (0.95)
Grinding	7	30 (0.02)	0.18 (0.9)	0.25 (1.32) <sup>†</sup>	0.17 (1.04) <sup>‡</sup>	0.6 (0.88)
Washing	5	44 (0.26)	0.1 (0.87)	0.23 (0.37)	1 (0.99)	1.33 (0.86)
Tank	7	33 (0.13)	0.12 (0.82)	0.7 (1.29) <sup>†</sup>	1.49 (1.43)	2.31 (1.29)
Central coolant system (CCS)	6	31 (0.04)	0.17 (0.67)	0.15 (1.57) <sup>†</sup>	ND	0.32 (1.02)
On conveyor belt	7	27 (Air)	0.02 (1.71)	ND	ND	0.02 (1.71)

MEA: monoethanolamine, DEA: diethanolamine, TEA: triethanolamine, ND: Not detected, RSD: relative standard deviation.

\*Boring (9), milling (8), drilling (4).

<sup>†</sup>No of samples not detected = 4 from grinding, 1 from tank and 4 from CCS.<sup>‡</sup>No of samples not detected = 3.

TEA. MEA may be lost to evaporation, although a certain amount was formed by conversion from either TEA or DEA. This trend was clearly detected for all the used fluids. Lessmann et al. [7] reported that current amine-containing products are characterized by a low level of MEA, although the source of the determination of this level was not specified.

The percentage of total EA that was in the used fluid relative to that in the fresh fluid ranged from 12% to 22%, with an average of 15%. This difference could be caused by losses due to both vaporization and dispersion into the air as mist. The change in EA concentration between the fresh and used the fluid could not be evaluated because there was no information on the dilutions.

### Airborne EA levels

Airborne EAs levels were measured from several machining operations and areas (Table 6). Airborne TEA was not detected in 13 samples that were taken from the central coolant system and near the conveyor belt, where no machining work was performed. DEA was detected to be 0.45 mg/m<sup>3</sup> from the only two samples. In contrast, MEA was found in all samples, regardless of the type of operation. There were metalworking operations with no TEA (three from seven samples in grinding operations) or DEA (four from seven samples in grinding operations, and one from seven samples in tank operations), even though machining work was performed. In terms of the total EA level, tank operations exhibited the highest level (2.31 mg/

m<sup>3</sup>), followed by washing (1.33 mg/m<sup>3</sup>), grinding (0.60 mg/m<sup>3</sup>), and machining (0.36 mg/m<sup>3</sup>).

## Discussion

EA-containing wbMWFs used as the coolant dissipate heat in the cutting zone by absorbing heat from the work-piece, chip, and tool. In order to increase metal removal rates, feed volumes and speeds must be increased. These increases result in elevated temperatures, which is the most critical limitation to a tool's life [8]. During high-speed metalworking operations, wbMWFs containing EAs may be altered due to the extreme heat generated on the work surfaces of the metal parts being machined.

EAs generally have low vapor pressure (at 20°C MEA = 0.404 torr, DEA < 0.01 torr, and TEA < 0.01 torr), which reduces the inhalation hazard in industry. Savonius et al. [3] pointed out that EAs are a minor constituent of the total chemical compounds involved in machining, but, especially if they are heated, there may be substantial exposure to EA vapors, which may induce asthma. In MWF-using industries, there are many machining operations that generate extreme temperatures and pressures. It is less well understood how, during machining operations, chemical additives in fresh fluids are converted, degraded, vaporized, and condensed.

This study has shown through experimental tests that conversion, condensation, and vaporization can occur among (or within) EAs contained in wbMWFs. Both airborne and fluid bulk EA levels may be influenced by these changes due to heating of the work-piece during machining operations. Our findings are applicable to machining operations in several aspects, as discussed below.

First, evaporation of MEA was found to increase with increasing temperatures, without condensation, while no vaporization of the other EAs (DEA and TEA) occurred. This result indicated that MEA in fluid may change to a vapor, even if it is not exposed to a high temperature, through the process of evaporation. MEA may therefore be vaporized even in those processes or areas without metalworking operations, where fluids are stored, circulated, refilled, or in a sump. This assumption is supported to some extent by the results of airborne EA levels. MEA was detected not only at the CCS and on the conveyor belt, where no metalworking operations were performed that generated high temperatures, but in all machining operations. Even if engineers handle operations or areas without machining or metalworking operations that generate mist, they can be exposed to airborne MEA. Further study is needed to compare airborne EA levels according to the type of machining operations, and to examine the relationship between EAs

and fluid mist levels.

Second, both DEA and TEA, with low vapor pressures (< 0.01 torr at 20°C), were found to condense as soon as they evaporated. This result indicated that both DEA and TEA in fluids were difficult to change into vapor through the process of vaporization alone. Thus, most of the airborne DEA and TEA could originate from fluid aerosol mist that was a result of fluid splashing from the machine, fluid applied to cool the cutting zone, and due to the use of air or aerosol-powered aspirating equipment to disperse the fluid and clean work pieces. Based on these results, machinists who are involved in machining operations that generate mist may be exposed to both DEA and TEA through fluid aerosols rather than via evaporation.

Third, both DEA and TEA may be converted into other EAs of lower molecular weight when they are exposed to heat generated during metalworking operations. Both MEA and DEA may be generated if a fluid bulk containing only TEA is exposed to machining operations that generate high temperatures through conversion of EAs with more alcohol groups, even if they were not originally included in the fresh fluid. This assumption is supported by the results showing that the three types of EA were detected in all the used fluids (Table 5, Table 6). We conclude that conversion of fresh fluid EAs with more alcohol groups into EAs with fewer alcohol groups may contribute to the increment of the latter EAs in the fluid and air, although the exact amounts converted were not determined in the present study. This conversion may depend on various factors, such as the EA fluid formulation, the temperatures encountered during machining, the cutting speed, and the type of machining process. As a result of the conversion reported in this study, fluid bulk EA levels could not be directly used to estimate and assess exposure to specific types of EAs, although the specific content based on the type of EA should nevertheless be indicated in the MSDS. Furthermore, MSDS results of this study indicated that the concentrations of functional groups, such as alkanolamines, amines, or amine complexes, were presented in terms of a percent range only, which is not sufficiently specific information for the assessment of health risks. This result is in agreement with the conclusion reached by Kenyon et al. [9] who found that the EA level in the bulk fluid was not listed specifically, but only in terms of the functional group name, such as alkanolamine, or as organic corrosion inhibitors, such as alkanolamine esters, aliphatic alkanolamines, alkanolamine carboxylates, etc. They reported the fresh bulk fluid concentrations of MEA (< limit of detection (LOD)-11%), DEA (< LOD-5%), and TEA (0.3-40%), and revealed little correlation between the type and level specified on the MSDS and those measured in the bulk fluids. The specific content based on the

type of EA should be indicated in the MSDS because the toxicity varies among these three types of EAs.

Finally, the proportion of each EA as a percentage of total EA was found to be different in the fresh fluid relative to the used fluid, indicating that the vaporization, condensation, and conversion occurring among the EAs may affect the combinations. The MEA percentage in fresh fluid (30% of total EA) was consistently higher than that in all the used fluids ( $n = 5$ , range 17.5-25.5%). The loss of MEA to either evaporation or formation of aerosols seemed to be higher than that added by conversion from TEA or DEA. The opposite trend was found for DEA, which represented a substantially higher percentage of total EA in the used fluid (12.4%) than in the fresh fluid (4%). As discussed above, conversion of TEA into DEA may be one of several factors resulting in this consistent increase of DEA in the used fluid. Based on the similar ratio for TEA between the fresh (66%) and used fluid (66.0-70.4 %), however, the amount converted may not be substantial. Until now, no study has reported not only the EA levels in the used fluid bulk, but also the relationship between the EA levels in the used and fresh fluids. In Germany, the permissible (residual) level of DEA in wbMWFs was set at 0.2% in 1993 because DEA may form carcinogenic N-nitrosamines. Slightly more recently, Lessmann et al. [9] reported that few samples contained DEA at the maximum concentration as a component in technical grade fluids.

The level of DEA in the fresh fluid we reviewed was found to be low or not detectable, which was comparable to levels of both MEA and TEA in two previous articles [8,9].

Although the use of DEA in wbMWFs was restricted because it may form carcinogenic N-nitrosamines, it has been found in fresh and used fluids, in some cases, at levels of more than 0.2% [9]. This study found that DEA levels were higher than 0.2% in most fresh and used fluids (Table 4, 5). Only elimination of EAs in fluid formulations would reduce respiratory and dermal effects and prevent exposure to formulated or endogenous carcinogens [10]. Efforts are being made to offer wbMWFs that are free of EAs. This suggestion could be beneficial based on the results of this study showing that TEA with three alcohol groups could be a generation source for EAs with two groups (DEA) or one group (MEA) in the used fluid.

### Limitations

A major limitation of this study is that we were unable to identify a specific temperature that leads to the conversion of EAs with more alcohol groups into EAs with fewer groups. In addition, the amounts converted could not be determined. The effects of vaporization, condensation, and conversion occurring among airborne EAs and fluid bulk EA levels could also not be

evaluated. Conversion rates and specificity and selectivity depend on the chemical kinetics of the mixture of EAs found in a given MWF product and, thus, upon time, composition, and temperatures achieved in the use conditions. The vaporization of EAs at concentrations of 1% in water was determined in an experimental apparatus described as a thermostat-controlled water bath. No other concentrations of the EAs were considered. Our study does not demonstrate that isothermal conditions existed throughout the vaporization bath. Nor does it demonstrate that vaporization rates are at all applicable under the very-different conditions under which the MWFs are used in the workplace. Formation and loss effects due to evaporation and chemical reaction could not be distinguished because chemical kinetics regarding the formation, destruction, and possible chemical equilibria involving MEA, DEA, and TEA were not studied. Furthermore, the recovery rate of MEA (average = 98.53 %, range = 95-104 %) failed to demonstrate that the rate should theoretically be greater than 100 % if DEA and TEA convert to EAs of lower molecular weights. A couple of reasons may have caused this result: the collection efficiency may have been low and some loss due to the evaporation of MEA may have occurred during sampling. Meanwhile, this result may indicate that the amount of MEA converted from DEA and TEA may not be great. To solve some of these limitations, it will be necessary to examine the relationship between the levels of each EA as a percentage of total EA in the air and used fluid, as well as in the fluid aerosol levels.

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